AIR QUALITY

DRYDEN

Annual Report, 1977

Ministry
of the
Environment

Ontario

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Annual Report, 1977

TECHNICAL SUPPORT SECTION
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CONTENTS

SUMMARY	1
INTRODUCTION	2
VEGETATION AND SOIL ASSESSMENT	2
SNOW SAMPLING	4
AIR MONITORING	5
PARTICULATE POLLUTANTS	5
Dustfall	5
GASEOUS POLLUTANTS	7
Sulphation Rate	7
Reduced Sulphur	8
ACKNOWLEDGEMENTS	9
REFERENCES	10
FIGURES AND TABLES	11-24

SUMMARY

The Ontario Ministry of the Environment has conducted air quality assessment investigations in Dryden since 1970. This report presents results of the 1977 programme, which included vegetation and soil studies, snow sampling, and air quality monitoring in the vicinity of a local kraft pulp mill and chlor-alkali plant.

Concentrations of mercury in vegetation, which fell sharply in 1976 following conversion of the chlor-alkali plant to a non-mercury process, showed a further moderate decline in 1977. Mercury levels in soil near the mill were slightly above normal and remained about the same as those recorded in 1975 and 1976.

Mercury in snow followed the same trend as that found in vegetation: a substantial decrease in 1976 and a more modest one in 1977. However, levels of calcium, sodium, and sulphate in snow remained well above current guidelines in an area around the mill. Black particles (black char or lignite) were also visible on the snow surface.

Dustfall frequently exceeded the monthly Ontario objective, particularly early in the year. Total dustfall and sulphate in dustfall both decreased significantly after emission controls were installed at the mill in April.

Sulphation rate measurements and continuous monitoring showed that unsatisfactory concentrations of total reduced sulphur (TRS) occurred in the town area. Highest TRS levels were about six times the acceptable limit. Analysis of wind direction data established that the local pulp mill was the principal source of TRS emissions.

INTRODUCTION

Since 1970, the Ontario Ministry of the Environment has conducted an air quality assessment programme in the vicinity of a 625 ton-per-day bleached kraft pulp mill and chlor-alkali chemical plant in the town of Dryden. Results of these investigations, encompassing vegetation and soil studies, snow sampling and air quality monitoring, have been described in detail in earlier reports (1,2). In 1977, the programme included a continuation of some parts of the vegetation and soil assessment work, and an additional snow sampling survey. Dustfall and sulphation rate measurements were made at six sites and, beginning in early February, total reduced sulphur was monitored continuously in the town centre.

VEGETATION AND SOIL ASSESSMENT

Vegetation and soil samples collected in 1975 near the pulp mill and chemical plant contained elevated levels of mercury. In 1976, following the termination of chlorine manufacture by the mercury-cell process in the chemical plant, mercury concentrations in foliage of nearby trees fell sharply. Mercury levels in soil from the same area showed no significant change.

In 1977, vegetation and soil was again collected for mercury analysis. At each site (Figure 1), triplicat samples of foliage were obtained from trembling aspen (*Populus tremuloides*) and Manitoba maple (*Acer negundo*) trees. Each sample, about 500 g (grams) fresh weight, was collected by manually trimming outside

leaf growth to about 6 m (metres) above ground on the sides of trees facing the source. Foliage was placed in perforated polyethylene bags and stored under refrigeration ($4^{o}C$) until processed in the Ministry's Thunder Bay laboratory. Sample material was dried in an oven at $80^{o}C$ for 30 hours, ground in a Wiley mill equipped with a 1-mm (millimetre) pore-size screen, then submitted for analysis, by ultraviolet atomic absorption, at the Ministry's Toronto laboratory. Triplicate soil samples were obtained with a stainless steel corer, 2.5 cm (centimetres) in outside diameter, from undisturbed areas at the sample locations. Before insertion of the corer, surface debris and loose organic matter were removed from the soil surface. Each core was separated into fractions representing depths of 0-5 and 0-10 cm, and any excess was discarded. At least 10 cores were pooled to form one sample, which was placed in a polyethylene bag to await processing in Thunder Bay. Sample material was spread on paper, air-dried for 48 hours, pulverized with a wooden mallet, coarse screened to remove stones and organic matter, then fine-screened through an 80-mesh sieve. Mercury determinations, at the Toronto laboratory, were performed by the same analytical technique used for foliage samples.

Mercury concentrations in vegetation and soil are summarized in Table 1, where values for 1975 and 1976 are also included for comparison. Near the mill, mercury in vegetation decreased moderately in 1977 compared with 1976, and very substantially compared with 1975, the last year the mercury-cell process was used in the chemical plant. In 1977, only one value exceeded the Ministry's current guideline of 100 ng/g (nanograms per gram),

dry weight. The 1977 data are plotted in Figure 2. Mercury in surface and subsurface soil (Table 1, Figures 3a and 3b) did not change significantly over the same period. Although average mercury levels in a few samples were above the guideline of 300 ng/g, the mercury content of Dryden soil was much lower than that in soil at equivalent distances from other mercury-cell chlor-alkali plants in Ontario (3,4). Mercury concentrations in Dryden vegetation and soils will be determined again in 1978.

SNOW SAMPLING

Snow sampling is often useful in assessing the kind, amount and extent of particulate contaminants near industrial sources of air pollution. Guidelines have been developed for concentrations of several elements in snow meltwater. Values exceeding the guidelines do not necessarily imply adverse environmental effects, but indicate that contaminant levels are significantly above those in unpolluted snow.

Duplicate samples were collected in early March from the same sites chosen for similar surveys in 1975 and 1976. Sample processing and analytical procedures were also the same (2). Results are presented in Table 2. Sodium and sulphate were significantly elevated, and calcium moderately elevated, in snow at locations near the mill area. Concentrations of all three contaminants substantially exceeded current guidelines (5 mg/l for calcium, 10 mg/l for each of sodium and sulphate) at many sites, and declined with increasing distance from the emission source. Calcium, sodium and sulphate levels were similar in 1975, 1976 and 1977. The 1977 samples were probably collected too soon after lime kiln emission controls were installed to show any benefits from the latter.

Mercury concentrations in snow have demonstrated a progressive decrease (Table 3) since the mercury-cell process was discontinued at the mill's chemical plant in late 1975. This improvement is clearly illustrated in Figures 4a and 4b, which compare mercury levels in snow in 1975 and 1977. The average decrease in the mercury between these years was 86 percent. Although all but one sample were within the guideline of 100 ng/l, the interpretation of the data are open to doubt because of melting conditions to which samples were exposed between the dates of collection and processing. Some of the mercury may have evaporated during this period.

Average snow depth was 47 cm on the date of sampling. About 25 cm of snow fell in the 10-day period before the survey. A deposit of black particulate matter, probably bark char or lignite, was found on the snow surface up to 1700 m from the mill. Some brownish particulate (sawdust?) was noted on snow just to the west of the pulp mill. The occurrence and distribution of visible contaminants was about the same in 1975, 1976 and 1977.

AIR MONITORING

PARTICULATE POLLUTANTS

Dustfall

Dustfall, one of the most visible kinds of air pollutants, consists of particulate matter which settles out from the atmosphere by gravity. It is measured by exposing open-top plastic jars to the air for 30 days and weighing the collected matter. Specific components of dustfall may also be determined by chemical analysis

or microscopic examination. Results are expressed in g/m^2 (grams per square metre) for 30 days. The Ontario air quality objectives for total dustfall are 7 g/m^2 for 30 days and 4.6 g/m^2, annual average. These values are equivalent to 20 and 13 tons per square mile which were, respectively, the monthly and annual objectives in use before conversion to metric units in 1977. All dustfall weight determinations and sulphate analyses were performed in the Ministry's Thunder Bay laboratory.

Dustfall levels for 1977 are given in Table 4 for six sites whose locations are shown in Figure 5. The monthly Ontario objective for total dustfall was exceeded frequently in the early months of the year, but not at all after August. Annual averages were highest near the mill (Figure 6) and lowest at station 61025, to the northeast. Dustfall at the latter site was the only one below the acceptable limit for the year. Sulphate was an important constituent of dustfall from January to March, but dropped sharply in April and later months following the installation of a new recovery furnace precipitator at the mill. Operation of this precipitator also resulted in a very satisfactory decrease in sodium and sulphate in the snow survey conducted in February, 1978, details of which will appear in the 1978 air quality report. For the 6-station survey, average dustfall in 1977, at 6.4 g/m^2, was down about 17 percent from the average of 7.7 g/m^2 in 1976. Further improvement is anticipated in 1978.

Large black particles, probably bark char, were often seen in dustfall jars exposed at stations 61011 and 61023, and were occasionally noted in jars at the more distant monitoring sites.

GASEOUS POLLUTANTS

Sulphation Rate

Sulphation rates provide an indication of the presence of sulphur-containing gases in the air. They are determined by exposing small plastic dishes, coated with lead dioxide, to the atmosphere for 30-day periods. Lead dioxide combines with reactive sulphur compounds to form lead sulphate. The quantity of sulphate formed is analytically determined and reported as mg $SO_3/100\ cm^2$/day (milligrams of sulphur trioxide per hundred square centimetres per day). Although the method is normally applied to estimate average sulphur dioxide concentrations, measurable sulphation rates may also be recorded if other reactive gases are present. In Dryden, air quality surveys with mobile equipment have shown that sulphur dioxide levels are negligible (1). Therefore, reduced sulphur compounds are considered to be the only reactive gases contributing to local sulphation rates. The air quality objective for sulphation rate was established in relation to long-term sulphur dioxide levels and cannot, therefore, be applied to the interpretation of sulphation rate data from Dryden.

Sulphation rate results for 1977 are presented in Table 5. Lowest rates were encountered in September and December. The pulp mill was closed for maintenance or inventory reduction during parts of both of these months. Highest averages, as expected, were recorded at sites closest to the mill (Figure 7).

Reduced Sulphur

Hydrogen sulphide (H_2S) and methyl mercaptan (CH_3SH) are principal components of a group of sulphur gases collectively known as "total reduced sulphur" (TRS). These compounds are commonly associated with emissions from kraft pulp mills and produce offensive odours at very low concentrations. If exposed to higher levels, some people may experience temporary respiratory irritation, and vegetation may be injured. A guideline of 27 ppb (parts per billion), hourly average, was recently established as the Ontario air quality objective for TRS in the vicinity of kraft pulp mills.

In 1977, TRS was continuously monitored for 11 months with a Philips model 9755 analyzer, at station 61026, about 600 m from the kraft mill. The data are summarized in Table 6 and in Figure 8. Concentrations of TRS exceeded the guideline during 272 hours, or about 4 percent of the total hours monitored. Lowest monthly average concentrations occurred in July and September, when the mill was shut down for substantial periods. The highest hourly reading was 164 ppb, about six times the maximum acceptable limit. Much higher levels would be expected closer to the mill. Analysis of TRS readings and wind direction for the months of February to October (Table 7) shows that at least 75 percent of all pollution readings could be attributed to emissions from the kraft mill. A higher-than-expected frequency (11 percent) of detectable TRS levels were associated with north and northeast winds. The occurrence of readings with wind from these directions may be due to the presence of an unrecognized source or may reflect differences between wind directions in the town and the airport, 8 km to the northeast.

ACKNOWLEDGEMENT

The assistance of staff of the Dingwall Medical Group in operating the TRS monitor at station 61026 is gratefully acknowledged.

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4. Temple, P.J. and S. N. Linzon. 1977. Contamination of vegetation, soil, snow and garden crops by atmospheric deposition of mercury from a chlor-alkali plant. Proc. 11th Ann. Conf. on Trace Substances in Envir. Health (In press).

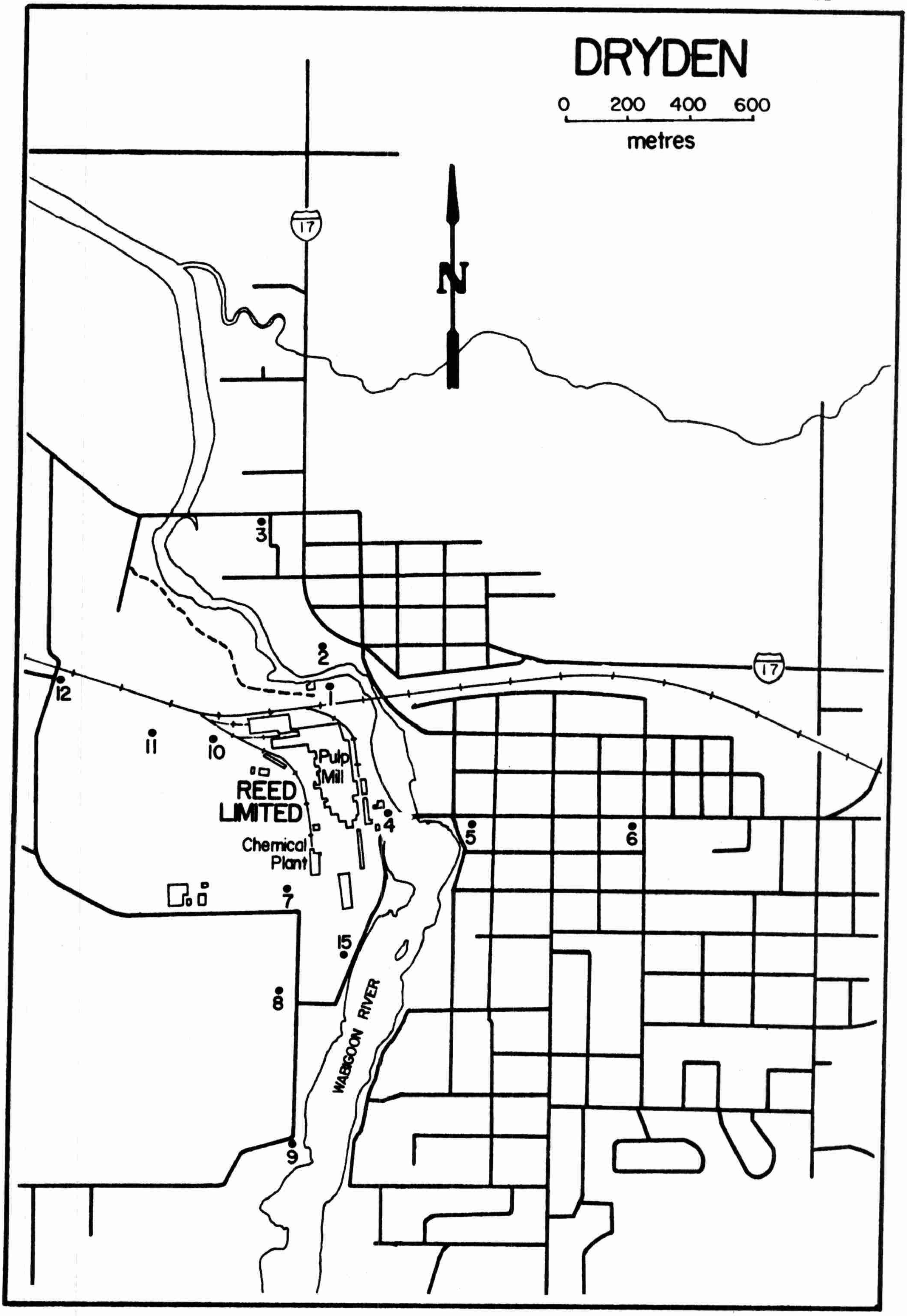

Figure 1. Vegetation and soil sampling sites, 1977.

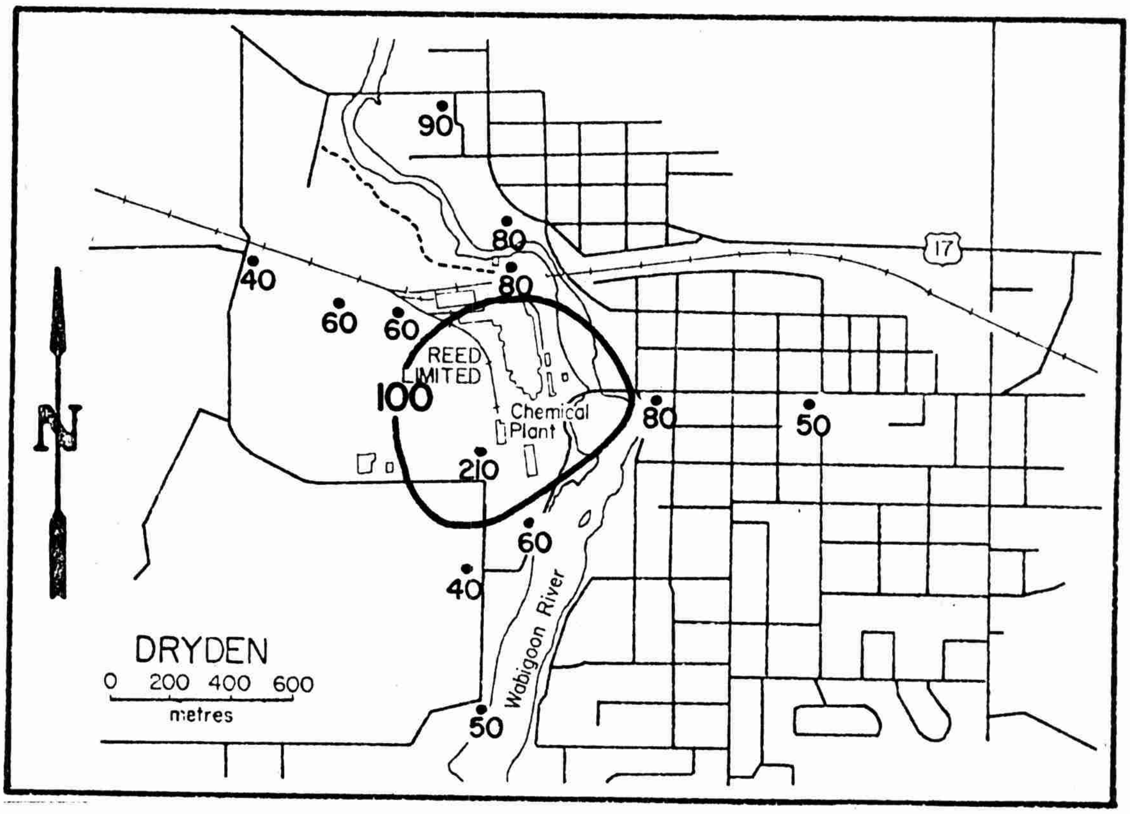

Figure 2. Average mercury levels (ng/g, dry weight) in trembling aspen and Manitoba maple foliage, August, 1977.

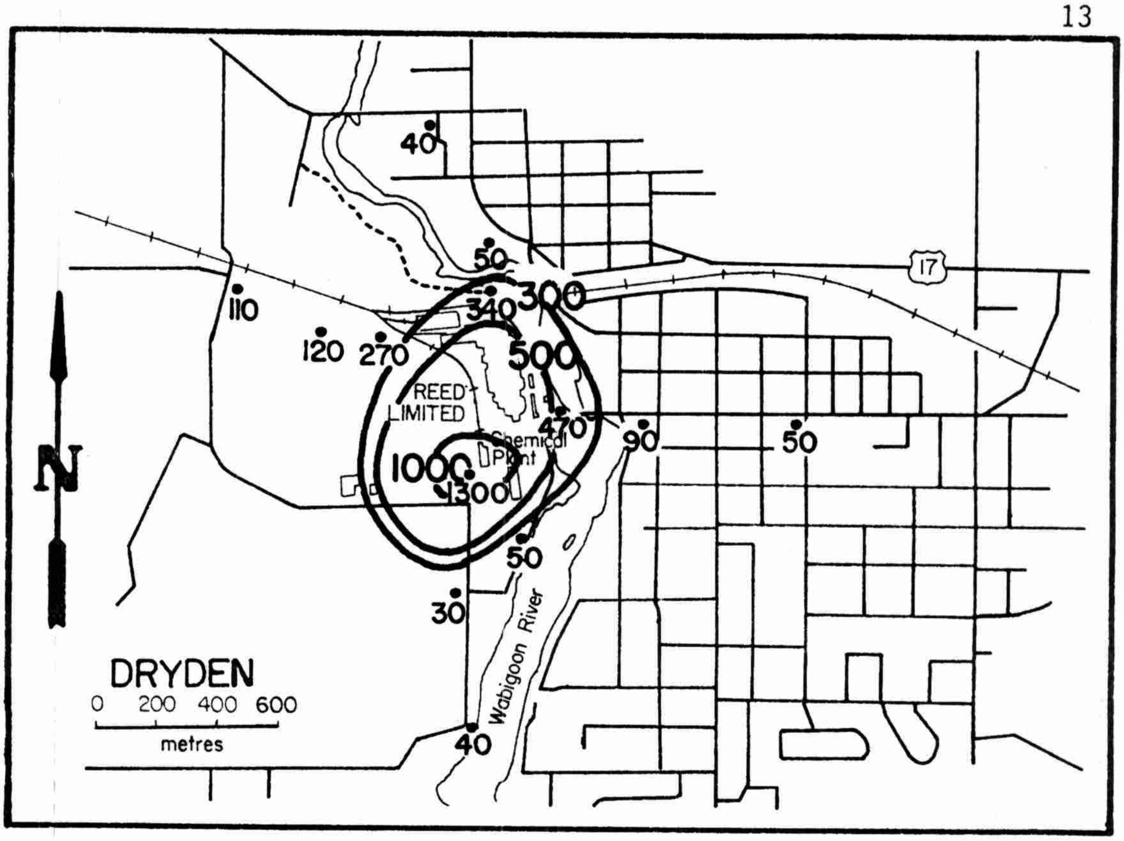

Figure 3a. Average mercury levels (ng/g, dry weight) in surface soil (0-5 cm), August, 1977.

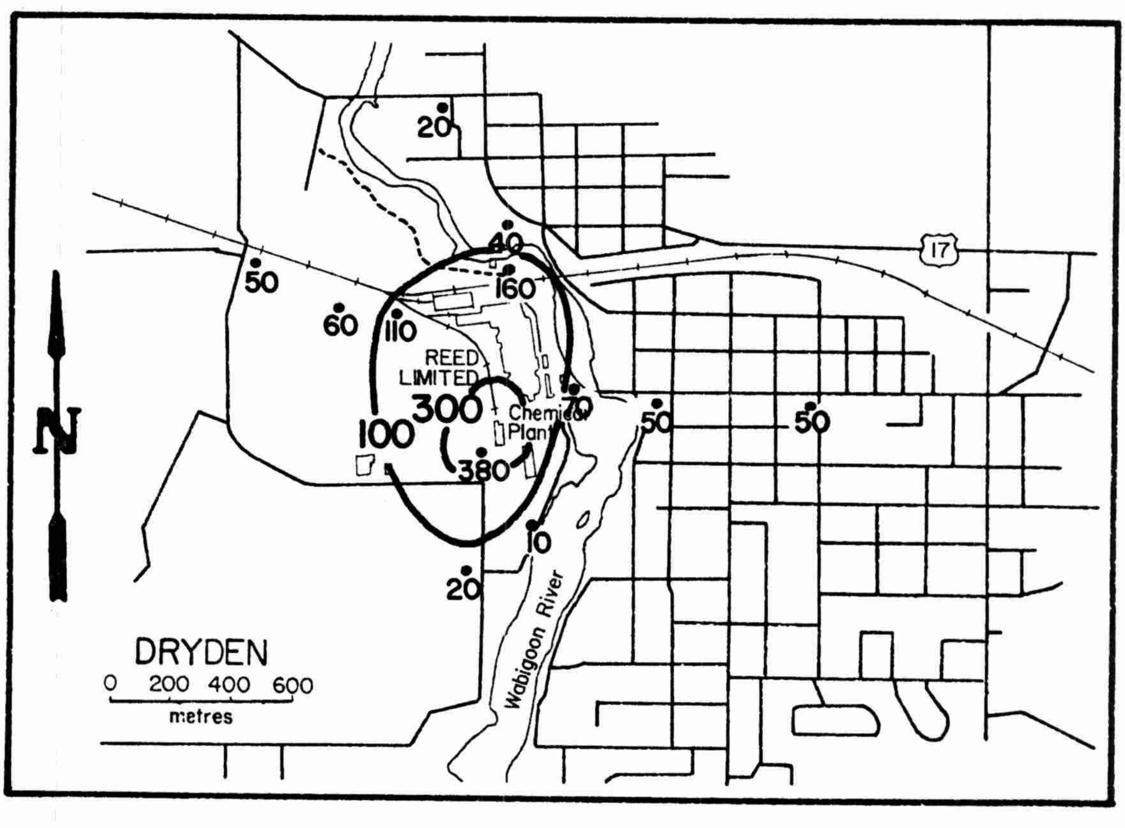

Figure 3b. Average mercury levels (ng/g, dry weight) in soil (5-10 cm), August, 1977.

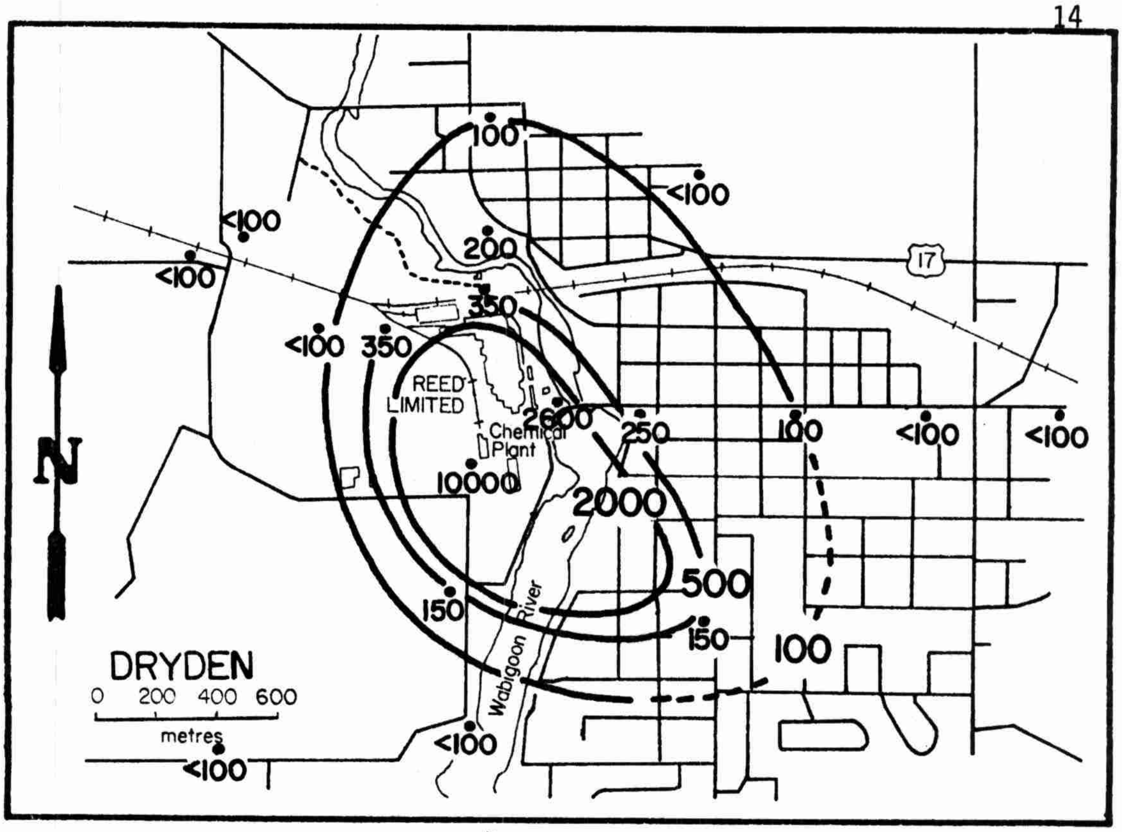

Figure 4a. Average concentrations of mercury (ng/l) in snow, January and March, 1975.

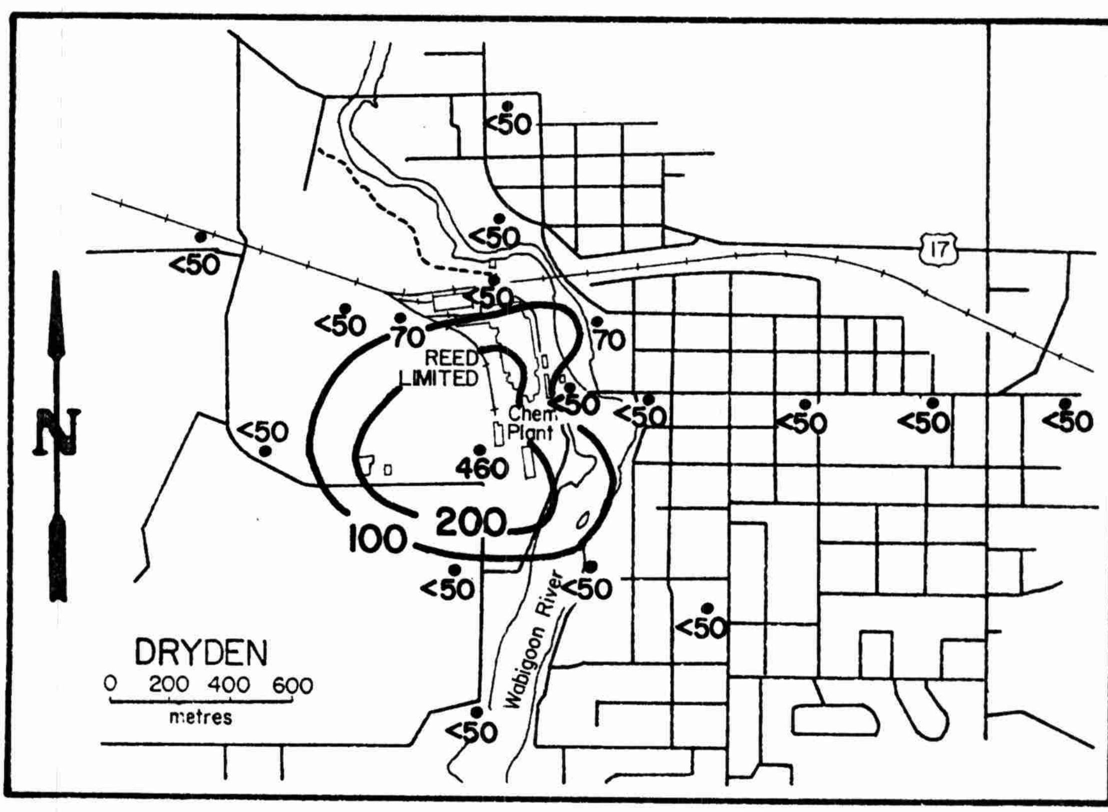

Figure 4b. Average concentrations of mercury (ng/l) in snow, March, 1977.

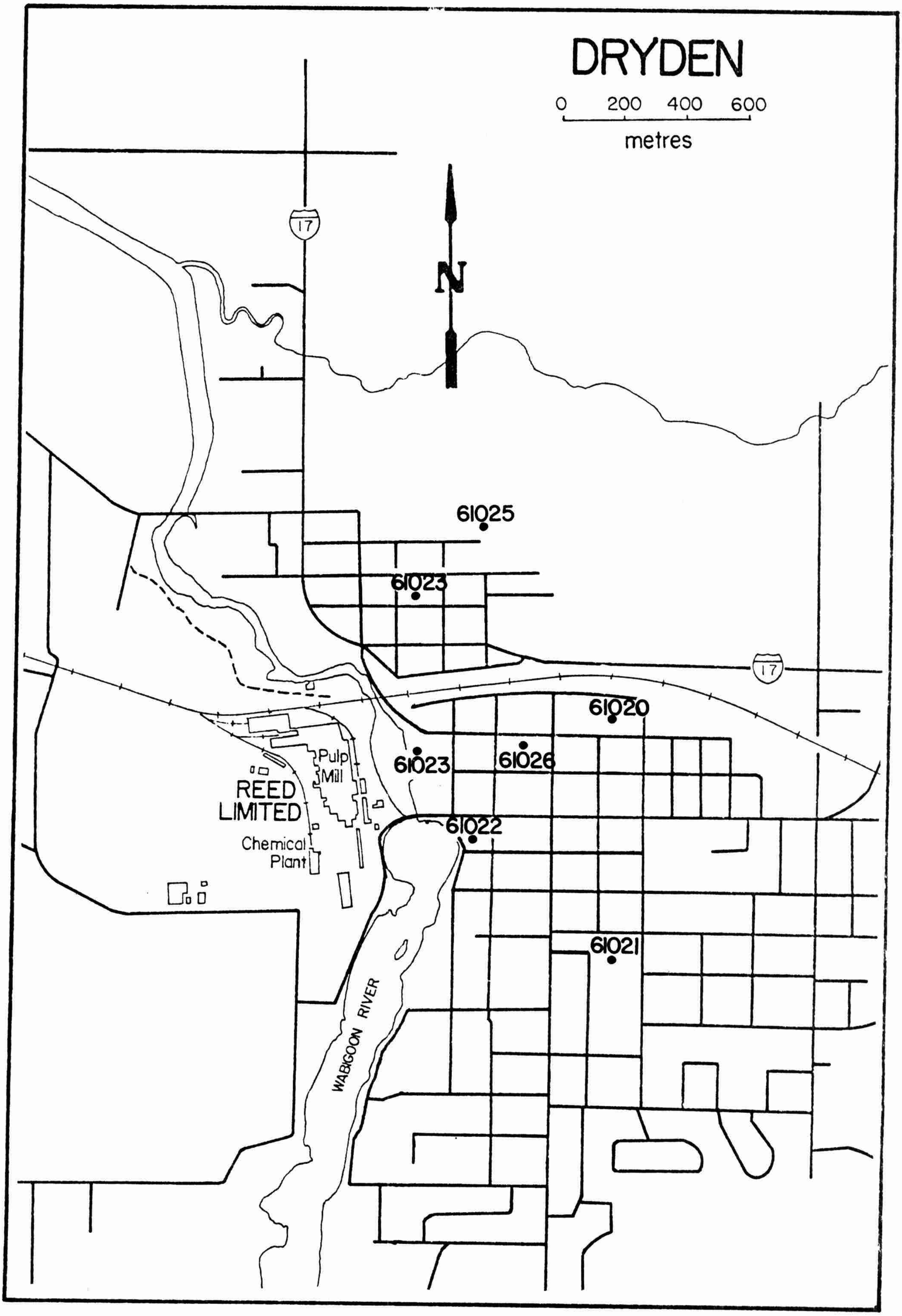

Figure 5. Air quality monitoring sites, 1977.

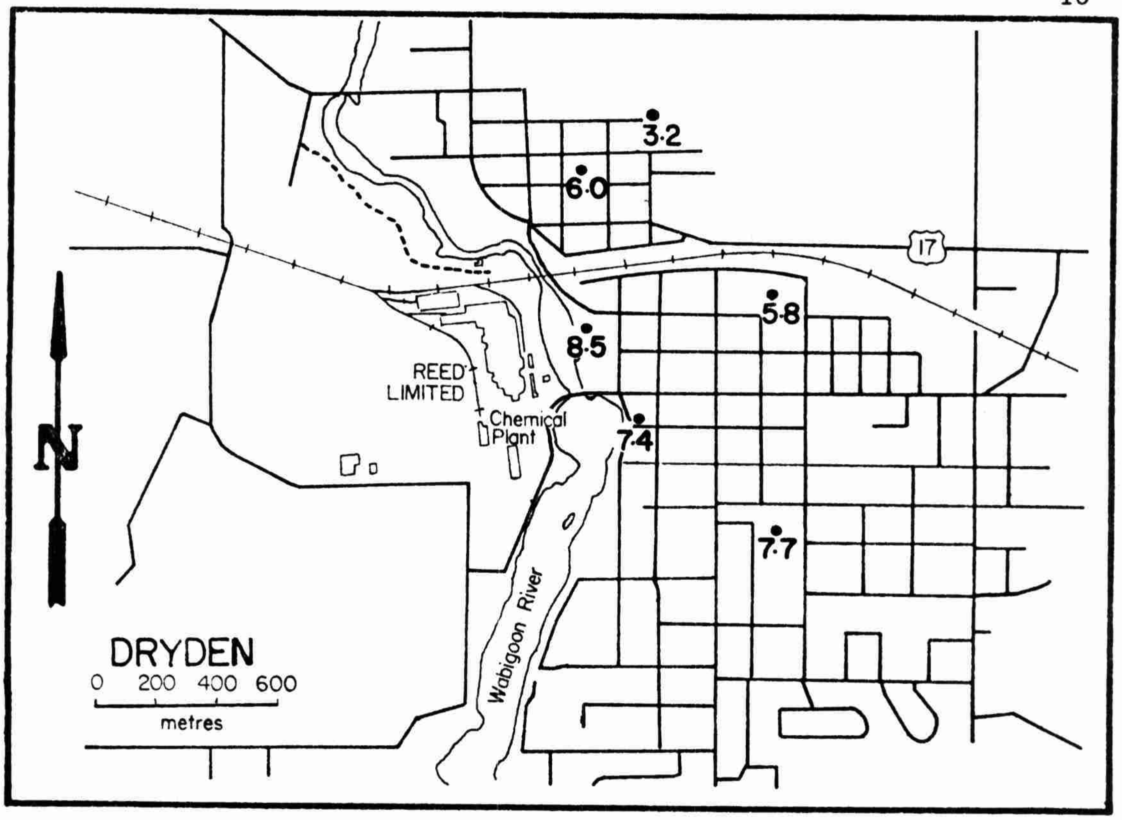

Figure 6. Average dustfall, 1977 ($g/m^2/30$ days).

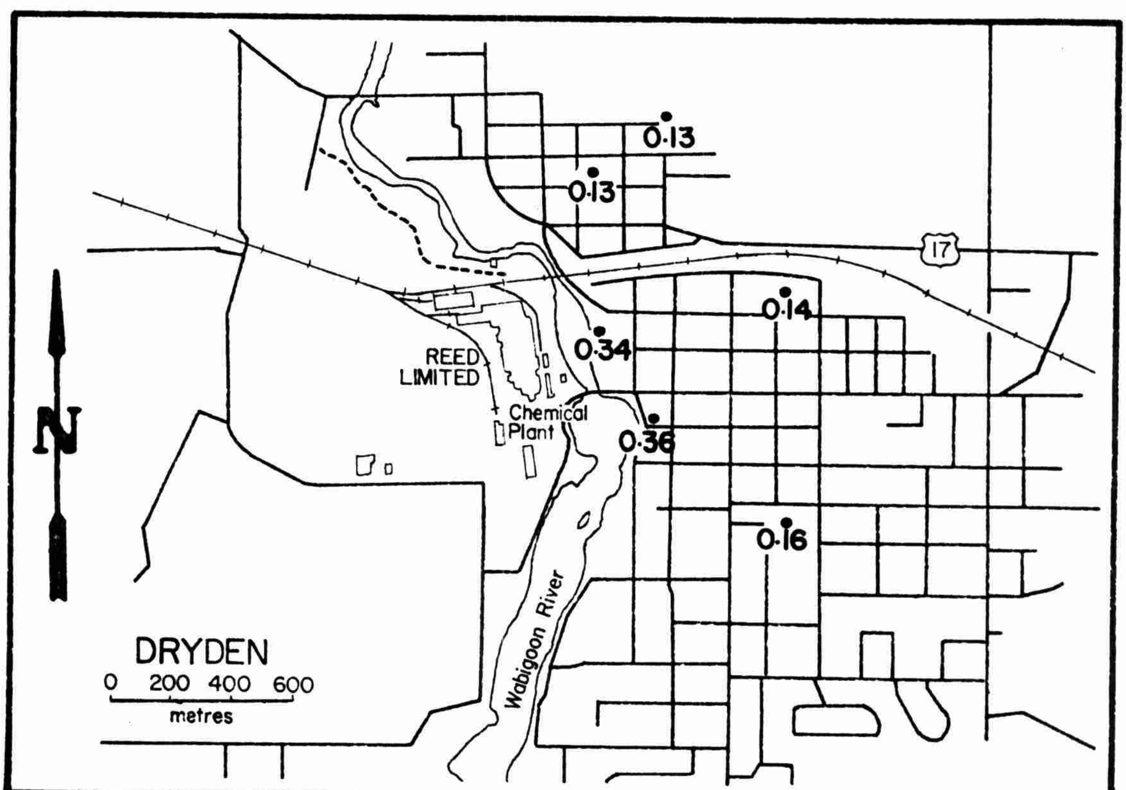

Figure 7. Average sulphation rates, 1977 (mg SO_3/ 100 cm^2/day).

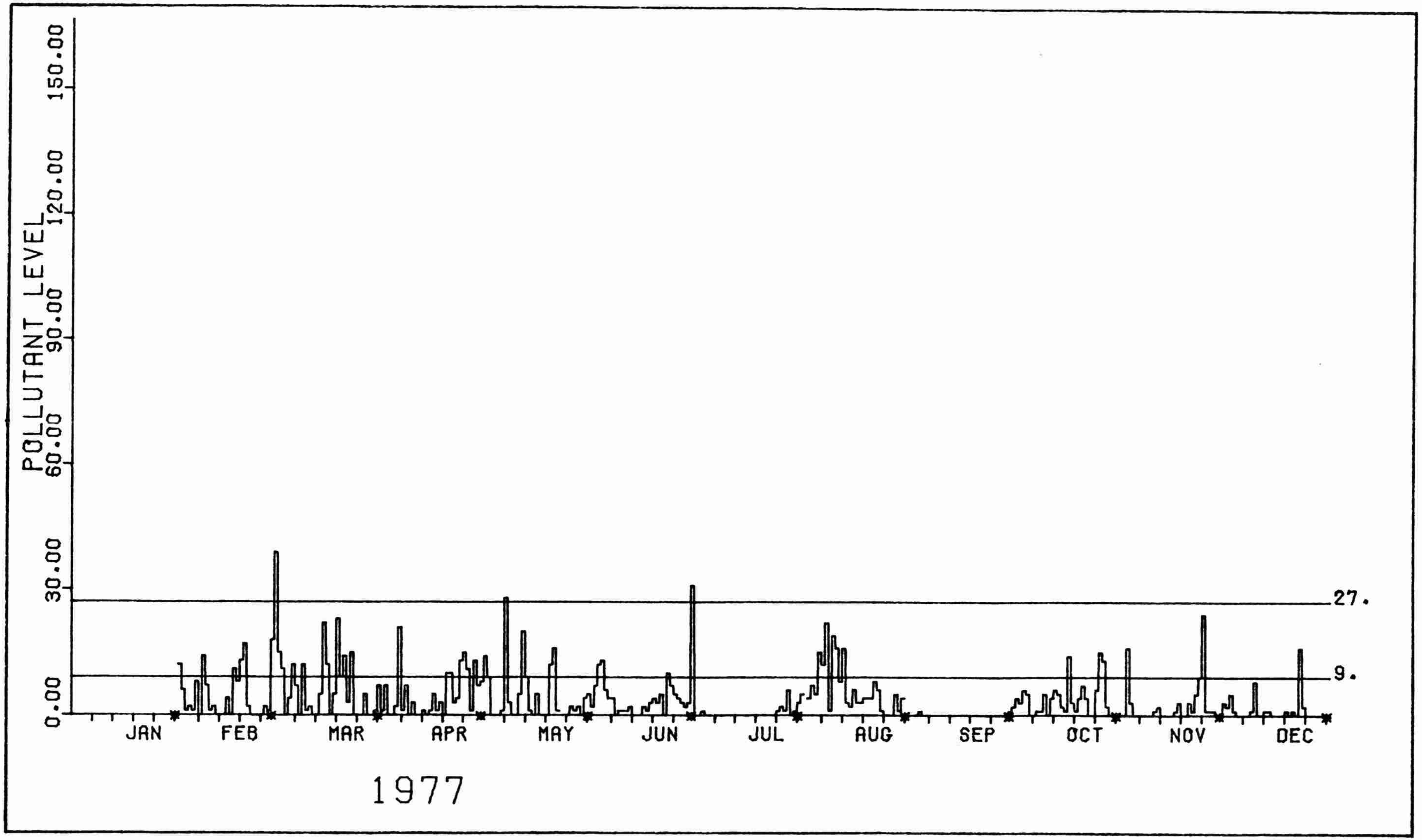

Figure 8. Daily mean TRS concentrations (parts per billion), station 61026, Dryden, 1977.

TABLE 1. Average mercury concentrations (ng/g, dry weight) in triplicate samples of vegetation[a] and surface soil in Dryden, 1975 to 1977.

Site	Distance (metres) and direction from source[b]	Vegetation 1975	Vegetation 1976	Vegetation 1977	Soil (0-5 cm) 1975	Soil (0-5 cm) 1976	Soil (0-5 cm) 1977
1	550 N	1840	100	80	140	50	340
2	700 N	1400	110	80	40	70	50
3	1105 N	510	180	90	30	30	40
4	270 NE				250	390	470
	405 NE				180		
	880 NNE				70		
5	520 ENE			80	110	130	90
6	880 E			50	140	50	50
	960 ENE				230		
15	300 SSE		120	60		370	50
	350 ESE				120		
	900 ESE				140		
7	110 SW	460	650	210	1170	1900	1300
	230 SW				670		
8	425 SSW	50	50	40	50	30	30
9	880 S	60	60	50	50	40	40
10	220 NW	510	160	60	200	340	270
11	480 WNW	380	90	60	180	300	120
12	975 WNW	140	30	40	70	100	110
Control	7700 ENE	20	20	15	50	10	50
Control	10700 WNW	20	40	20	50	40	20

[a]Trembling aspen foliage throughout, except at sites 5 and 6, where Manitoba maple foliage was collected.

[b]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.

TABLE 2. Average levels of calcium, mercury, sodium, sulphate and pH in snow collected in Dryden, March, 1977.

Distance (metres) and direction from source[a]	Calcium (mg/l)	Mercury (ng/l)	Sodium (mg/l)	Sulphate (mg/l)	pH
350 N	6	< 50	26	67	8.4
575 N	2	< 50	16	36	6.4
865 N	2	< 50	10	19	6.2
1455 N	1	< 50	4	7	5.4
2015 N	1	< 50	2	4	4.4
320 NE	16	70	48	86	8.8
930 NE	1	< 50	14	34	5.8
190 E	23	< 50	12	20	9.4
415 E	9	< 50	60	122	8.4
945 E	2	< 50	11	26	5.2
1325 E	2	< 50	8	18	5.2
1735 E	< 1	< 50	2	6	4.2
990 SE	2	< 50	24	57	6.1
655 SSE	6	< 50	95	205	7.3
1090 S	1	< 50	6	18	4.9
1410 S	2	< 50	28	75	6.6
255 SSW	16	460	12	25	9.5
690 SSW	4	< 50	19	52	6.2
1500 SW	2	< 50	5	11	5.7
870 WSW	6	< 50	14	26	8.1
300 W	8	70	42	82	9.0
550 W	2	< 50	11	26	7.0
1100 WNW	1	< 50	6	14	6.6
1500 WNW	2	< 50	4	9	5.6
2000 WNW	< 1	< 50	2	4	4.6
1000 NW	1	< 50	5	11	5.2
10700 WNW	1	< 50	< 1	< 1	3.6
7700 ENE	< 1	< 50	< 1	2	4.4

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.

TABLE 3. Average concentrations of mercury (ng/l) in snow collected in Dryden in 1975, 1976 and 1977.

Distance (metres) and direction from source[a]	1975	1976	1977	Percent decrease 1975 to 1977
350 N	350	300	< 50	93
575 N	200	80	< 50	88
865 N	100	60	< 50	75
1455 N	< 100	< 50	< 50	-
2015 N	< 100	< 50	< 50	-
320 NE	-	110	70	-
930 NE	< 100	< 50	< 50	-
190 E	2600	830	< 50	99
415 E	250	150	< 50	90
945 E	100	60	< 50	75
1325 E	< 100	< 50	< 50	-
1735 E	< 100	< 50	< 50	-
990 SE	150	100	< 50	83
655 SSE	-	60	< 50	-
1090 S	< 100	< 50	< 50	-
1410 S	< 100	< 50	< 50	-
255 SSW	10000	570	460	95
690 SSW	150	< 50	< 50	83
1500 SW	< 100	< 50	< 50	-
870 WSW	-	< 50	< 50	-
300 W	350	90	70	80
550 W	< 100	80	< 50	-
1100 WNW	< 100	< 50	< 50	-
1500 WNW	< 100	< 50	< 50	-
2000 WNW	< 100	< 50	< 50	-
1000 NW	< 100	90	< 50	-
10700 WNW	< 100	< 50	< 50	-
7700 ENE	< 100	< 50	< 50	-

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.

TABLE 4. Total dustfall and soluble sulphate in dustfall, Dryden, 1977.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
			Total dustfall ($g/m^2/30$ days)												
61020	Kirkpatrick/Queen	895 ENE	5.8	3.2	7.8[b]	7.0	9.5	7.1	6.9	6.6	-	3.4	1.0	-	5.8
61021	Casimir/St. Charles	1010 ESE	12.6	6.4	19.0	5.8	6.7	6.4	9.4	4.6	4.6	-	1.1	-	7.7
61022	Earl/Albert	430 ESE	11.6	11.9	11.1	8.0	9.5	10.5	4.6	5.6	3.7	3.1	2.2	-	7.4
61023	King/Wabigoon River	305 NE	11.7	7.9	20.8	8.6	-	-	7.6	7.9	5.0	5.1	1.5	-	8.5
61024	Mary/Florence	735 NNE	5.3	4.0	9.9	8.5	4.9	13.1	5.8	4.2	3.8	2.7	3.6	-	6.0
61025	Park/Second	960 NNE	2.4	1.8	8.3	3.4	4.4	-	4.3	2.7	1.5	1.1	1.6	-	3.2
			Soluble sulphate in dustfall ($g/m^2/30$ days)												
61020	Kirkpatrick/queen	895 ENE	2.2	1.5	3.0	0.5	1.0	0.6	0.2	0.5	-	0.2	0.1	<0.1	1.0
61021	Casimir/St. Charles	1010 ESE	3.1	2.0	3.3	0.6	0.7	0.3	0.2	0.3	0.2	-	0.2	-	1.0
61022	Earl/Albert	430 ESE	2.2	6.4	4.9	0.7	0.7	0.4	0.1	0.2	0.1	0.1	0.2	0.1	1.3
61023	King/Wabigoon River	305 NE	1.9	2.9	7.9	0.6	-	-	0.2	0.4	0.1	0.2	0.2	0.1	1.4
61024	Mary/Florence	735 NNE	1.5	1.9	4.7	0.4	0.5	0.3	0.1	0.1	0.1	0.1	0.2	0.2	0.8
61025	Park/Second	960 NNE	0.7	1.0	2.9	0.2	0.6	-	0.1	0.2	0.1	0.1	0.1	<0.1	0.5

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft mill.
[b]Values above air quality objectives of 7.0 (monthly) or 4.6 (annual average) are underlined.

TABLE 5. Sulphation rate (mg SO_3/100 cm^2/day), Dryden, 1977.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
61020	Kirkpatrick/Queen	895 ENE	.16	.14	.14	.12	.13	.17	.18	.16	.07	-	.14	.10	.14
61021	Casimir/St. Charles	1010 ESE	.29	.14	.14	.12	.12	.20	.18	-	.10	.16	.17	-	.16
61022	Earl/Albert	430 ESE	.70	.29	.23	.20	.22	.62	.38	.92	.10	.33	.19	.11	.36
61023	King/Wabigoon River	305 NE	.59	.57	.47	.29	.35	.30	.23	.70	.14	.13	.24	.10	.34
61024	Mary/Florence	735 NNE	.08	.07	.19	.11	.10	.13	.26	.13	.09	.25	.11	.05	.13
61025	Park/Second	960 NNE	.08	.07	.19	.10	.11	.13	.18	.17	.07	.29	.11	.05	.13

[a]Source arbitrarily designated as recovery furnace stack, Reed Limited kraft mill.

TABLE 6. Distribution of total reduced sulphur readings (ppb, hourly averages) at station 61026, Dryden, 1977.

	Days	Number of readings for concentrations of:						Maximum value	
Month	of data	0-10	11-27	28-50	51-100	101-200	200	Hourly	Daily
Jan			N O	D A T A					
Feb	28	541	61	18	5	1	0	164	18
Mar	31	589	65	41	22	1	0	127	39
Apr	30	580	55	24	8	2	0	112	21
May	30	590	38	34	12	0	0	90	28
Jun	30	573	61	17	7	0	0	89	31
Jul	26	574	3	0	2	0	0	74	6
Aug	29	542	69	19	12	2	0	130	22
Sep	28	628	4	2	0	0	0	49	1
Oct	30	603	52	9	7	1	0	162	15
Nov	30	667	19	11	8	0	0	86	24
Dec	31	709	17	6	1	0	0	88	16
Year	323	6596	444	181	84	7	0	164	39

TABLE 7. Directional distribution of hourly readings of total reduced sulphur (TRS) at station 61026, Dryden, 1977[a].

Wind direction[b]	Number of hours when TRS was monitored	Average concentration (ppb) when TRS was monitored
N	131	6
NE	73	8
E	32	7
SE	32	3
S	86	5
SW	466	20
W	500	14
NW	416	10
Calm	102	13

[a]For the months of February to October, inclusive. Wind data for November and December not available.

[b]Measured 10 m above ground at Dryden airport.